

the squares of the phonon frequencies. As $q \rightarrow 0$, the eigenvalues for the acoustic branches are of the order q^2 . We need to apply first-order perturbation theory to $C^{(2)}$ and second-order perturbation theory to $C^{(1)}$. By comparing the phonon equations to order q^2 with the equation of elastic waves,⁵ we obtain the elastic constants

$$c_{\alpha\gamma, \beta\lambda} = [\alpha\beta, \gamma\lambda] + [\beta\gamma, \alpha\lambda] - [\beta\lambda, \alpha\gamma] + (\alpha\gamma, \beta\lambda), \quad (3.11)$$

with the equilibrium condition

$$[\beta\gamma, \alpha\lambda] = [\alpha\lambda, \beta\gamma], \quad (3.12)$$

where

$$[\alpha\beta, \gamma\lambda] = (2\Omega_0)^{-1} \sum_{\kappa\kappa'} (M_\kappa M_{\kappa'})^{1/2} C_{\alpha\beta\gamma\lambda}^{(2)}(\kappa\kappa') \quad (3.13)$$

and

$$(\alpha\gamma, \beta\lambda) = -\Omega_0^{-1} \sum_j [\omega(O_j)]^{-2} \times \left[\sum_{\kappa\kappa' \alpha'} w_{\alpha'}(\kappa' | O_j) C_{\alpha'\alpha\gamma}^{(1)}(\kappa'\kappa) M_\kappa^{1/2} \right]$$

$$\times \left[\sum_{\kappa''\kappa'''\alpha''} w_{\alpha''}(\kappa'' | O_j) C_{\alpha''\beta\lambda}^{(1)}(\kappa''\kappa''') M_{\kappa'''}^{1/2} \right]. \quad (3.14)$$

$\omega(O_j)$ and $w_\alpha(\kappa | O_j)$ denote the frequency and polarization vector of J th optical mode at $\vec{q}=0$.

When a complex crystal is subjected to a homogeneous strain, the sublattices may move relative to one another. $(\alpha\gamma, \beta\lambda)$ represents the contribution of such effects to the elastic constant. In Eq. (3.14), we have put it in a more explicit form than Born and Huang.⁵

In simple metals with one atom per unit cell and conduction electrons nearly free, some of the terms considered here are not important. For example, $(\alpha\gamma, \beta\lambda)$ vanishes. We shall see, however, in the following paper that for an intermetallic compound such as Nb_3Sn , careful inclusion of such terms from a general theory is essential to an understanding of its lattice dynamics and crystal instabilities.

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Theory of Lattice Dynamics of Nb_3Sn -Type Compounds*

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We present a method of calculating electron screening in the tight-binding approximation and constructing the dynamical matrix for the β -W compounds. We show that, in the cubic phase, no long-wavelength optical mode is temperature dependent except Γ_{12} which has a weak temperature variation. By the method of long waves, we calculate the elastic constants, particularly $c_{11} - c_{12}$, as a function of temperature, obtaining a fair agreement with experiment. We infer that the cubic to tetragonal phase transition is due to the instability of the $c_{11} - c_{12}$ shear mode, associated with which is a tetragonal distortion of Γ_{12} symmetry, in agreement with the neutron-scattering experiment of Shirane and Axe.

I. INTRODUCTION

A number of intermetallic compounds A_3B of β -tungsten (A-15) structure have very high superconducting transition temperatures and undergo a structural phase transition (from cubic to tetragonal) at low temperatures. These have been the subject of intensive experimental and theoretical investigations.¹

The feature of interest to us here is the unusual temperature dependence of the phonon properties. The temperature dependence of the elastic

constants has been measured for V_3Si ,² V_3Ge ,³ and Nb_3Sn .^{4,5} Neutron measurements have recently been carried out for V_3Si ⁶ and Nb_3Sn .^{7,8} There also have been several calculations of the elastic constants^{1,9-11} and the phonon frequencies.¹²⁻¹⁴

In this paper, we show how, given a tight-binding model for the d electrons, we can calculate from first principles the phonon spectrum (Sec. II). In particular, we give a careful treatment of the screening of the effective ion interaction by d as well as s electrons, in contrast to previous

works where this is neglected^{9-11,13,14} or treated in an inappropriate approximation.¹² We examine the temperature dependence of the long-wavelength optical modes in the cubic phase and calculate the temperature dependence of the elastic constants (Sec. III). In the latter, we include the effects of sublattice motion which have been neglected in Refs. 9-11. We conclude that no long-wavelength optical modes become unstable on cooling (Sec. IV). The cubic-to-tetragonal phase transition is due to the $c_{11} - c_{12}$ shear instability, which, nevertheless, because of coupling to the Γ_{12} optical mode, can cause a tetragonal distortion of Γ_{12} symmetry, as shown to be the case in Nb₃Sn by neutron scattering.⁷ A summary of the conclusions of this work has been given.¹⁵

II. ELECTRON SCREENING

A. Model for Band Structure

For a calculation of the electron screening, we need the energy and wave function of the electron. In the A_3B compounds of β -W structure, A atoms are invariably transition elements. We treat the d electrons from A atoms in the tight-binding approximation.¹⁶ The s and p conduction electrons are treated in the nearly-free-electron approximation.

The distribution of atoms in a unit cell is depicted in Fig. 1. The index κ is used to label the atoms in the cell. For the band structure, it is also convenient to label the atoms by $(\lambda\nu)$, where λ is the Cartesian direction and $\nu = \pm$. Thus, $(\lambda\nu) = (2\pm)$ means atoms $\kappa = 3, 4$, respectively.

In the tight-binding approximation used here,¹⁶ the bandwidth of the d band is due entirely to the overlap of nearest neighbors of A atoms, i. e., atoms in the same chain. The d bands are shown schematically in Fig. 2. The bands are independent of components of the wave vector not in the direction shown. m denotes the magnetic quantum number. The bandwidths are of the order of

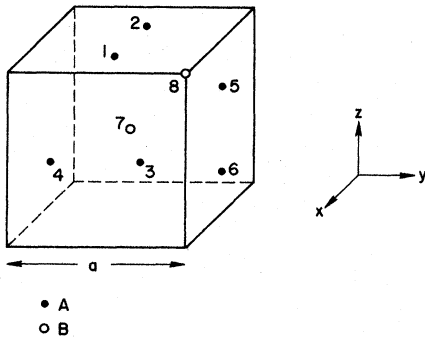


FIG. 1. Arrangement of atoms of an A_3B compound in the unit cell.

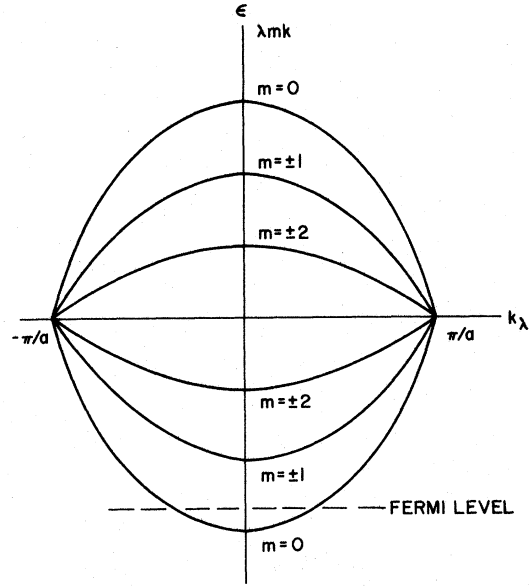


FIG. 2. Schematic diagram for the d bands.

several eV. The Fermi level lies near (of the order of 10^{-2} eV) one of the band edges where the density of states has a very high peak. This feature is confirmed by the result of the calculation by Goldberg and Weger¹⁶ It was first proposed by Clogston and Jaccarino¹⁷ to explain the temperature dependence of the electronic properties.

For simplicity, in this paper, we take the Fermi level to be near the bottom of the lower $m = 0$ band and neglect the other bands. The formalism we develop below can be straightforwardly extended to the other cases. Thus, the d bands now consist of three sets of $m = 0$ bands given by

$$\mathcal{E}_{\lambda\vec{k}} = 2J \cos \frac{1}{2} a k_{\lambda}, \quad (2.1)$$

where a is the lattice constant.

The associate wave function is given by

$$\psi_{\lambda\vec{k}}(\vec{r}) = (2N)^{-1/2} \sum_{l\nu} e^{i\vec{k}\cdot\vec{x}_{l\nu}} \varphi_{\lambda}(\vec{r} - \vec{x}_{l\nu}), \quad (2.2)$$

where $\vec{x}_{l\nu}$ is the position of $(\lambda\nu)$ atom in the l unit cell, N is the number of unit cells, and $\varphi_{\lambda}(\vec{r})$ is the $m = 0$ component of the atomic d wave function in Slater form:

$$\varphi_{\lambda}(\vec{r}) = (s^7/18\pi)^{1/2} (3\gamma_{\lambda}^2 - \gamma^2) e^{-sr}. \quad (2.3)$$

B. Proper Polarization Part

Consider the proper polarization part in the random-phase approximation (RPA). It is given by¹⁸

$$\bar{\chi}(\vec{q} + \vec{G}, \vec{q} + \vec{G}'; \omega) = \Omega^{-1} \sum_{\nu\nu'\vec{k}} \langle \nu\vec{k} | e^{-i(\vec{q} + \vec{G})\cdot\vec{r}} | \nu'\vec{k} + \vec{q} \rangle \times \langle \nu'\vec{k} + \vec{q} | e^{i(\vec{q} + \vec{G}')\cdot\vec{r}} | \nu\vec{k} \rangle$$

$$\times (n_{\nu, \vec{k}+\vec{q}} - n_{\nu, \vec{k}}) / (\mathcal{E}_{\nu, \vec{k}+\vec{q}} - \mathcal{E}_{\nu, \vec{k}} - \omega), \quad (2.4)$$

where \vec{q} is the wave vector confined to the first Brillouin zone, \vec{G} and \vec{G}' are the reciprocal-lattice vectors, ω is the frequency of the disturbance (i. e., phonon wave), and $n_{\nu, \vec{k}}$ is the occupation number. The part in Eq. (2.4), $\tilde{\chi}_s(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$, which involves transitions between s, p bands only is given in the free-electron approximation¹⁸ and are diagonal, i. e., nonvanishing only for $\vec{G} = \vec{G}'$. We neglect the transitions between the s, p bands and the d bands since the matrix elements for these transitions are smaller than those for the $d-d$ transitions. For the same reason, the most important $d-d$ transitions are those between the same d band. The transitions between different d bands are neglected.

By using the tight-binding wave function (2.2) and neglecting the smaller overlap terms, we obtain the matrix element

$$\begin{aligned} \langle \lambda \vec{k} | e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} | \lambda' \vec{k} + \vec{q} \rangle &= \delta_{\lambda\lambda'} S_\lambda(\vec{G}) \Psi_\lambda(\vec{q} + \vec{G}) \\ &= \delta_{\lambda\lambda'} F_\lambda(\vec{q}, \vec{G}), \end{aligned} \quad (2.5)$$

where

$$S_\lambda(\vec{G}) = \frac{1}{2} \sum_{\nu} e^{-i\vec{G}\cdot\vec{x}_{\lambda\nu}} \quad (2.6)$$

and

$$\Psi_\lambda(\vec{q} + \vec{G}) = \int d\vec{r} |\varphi_\lambda(\vec{r})|^2 e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}. \quad (2.7)$$

The d -electron contribution to the polarization (2.4) is thus

$$\tilde{\chi}_d(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \sum_{\lambda} \theta_\lambda(\vec{q}) F_\lambda(\vec{q}, \vec{G}) F_{\lambda'}^*(\vec{q}, \vec{G}'), \quad (2.8)$$

where

$$\theta_\lambda(\vec{q}) = \Omega^{-1} \sum_{\vec{k}} (n_{\lambda, \vec{k}+\vec{q}} - n_{\lambda, \vec{k}}) / (\mathcal{E}_{\lambda, \vec{k}+\vec{q}} - \mathcal{E}_{\lambda, \vec{k}} - \omega). \quad (2.9)$$

Spin degeneracy is understood.

We go a little beyond RPA by excluding from Eq. (2.8) the term which corresponds to the interaction term of two d electrons of same spin on the same atomic site. In this way, we have included the most important exchange effect in a narrow band.

C. Dynamical Matrix

The effective ion-ion interaction depends on the electronic-density response function¹⁹ $\chi(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$, given by the matrix equation

$$\chi = \tilde{\chi} + \tilde{\chi} v \chi, \quad (2.10)$$

where $v(\vec{q} + \vec{G})$ is the Coulomb interaction.

It is convenient to introduce the inverse dielectric function ϵ^{-1} defined by

$$\chi = \tilde{\chi} \epsilon^{-1}. \quad (2.11)$$

It also satisfies a matrix equation of the same form as Eq. (2.10),

$$\epsilon^{-1} = 1 + v \tilde{\chi} \epsilon^{-1}. \quad (2.12)$$

Since the kernel $\tilde{\chi}$ has a part $\tilde{\chi}_s$ which is diagonal and a part $\tilde{\chi}_d$ which is separable, the inversion can be easily carried out.²⁰ The effect of the s, p electrons is to screen the Coulomb interaction to become

$$v_s(\vec{q} + \vec{G}) = v(\vec{q} + \vec{G}) / \epsilon_s(\vec{q} + \vec{G}), \quad (2.13)$$

where

$$\epsilon_s(\vec{q} + \vec{G}) = 1 - v(\vec{q} + \vec{G}) \tilde{\chi}_s(\vec{q} + \vec{G}, \vec{q} + \vec{G}). \quad (2.14)$$

The screening by d electrons is given by ϵ_d^{-1} defined by

$$\epsilon_d^{-1} = \epsilon_d^{-1} \epsilon_s^{-1}. \quad (2.15)$$

Because of the separable form of Eq. (2.8), Eq. (2.12) for ϵ_d^{-1} becomes

$$\begin{aligned} \epsilon_d^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= \delta_{\vec{G}, \vec{G}'} + v_s(\vec{q} + \vec{G}) \sum_{\lambda} \theta_\lambda(\vec{q}) F_\lambda(\vec{q}, \vec{G}) \\ &\quad \times \sum_{\lambda'} F_{\lambda'}^*(\vec{q}, \vec{G}') \epsilon_d^{-1}(\vec{q} + \vec{G}', \vec{q} + \vec{G}'). \end{aligned} \quad (2.16)$$

Let X be the 3×3 matrix with elements

$$X_{\lambda\lambda'}(\vec{q}) = \sum_{\vec{G}} F_{\lambda'}^*(\vec{q}, \vec{G}) v_s(\vec{q} + \vec{G}) F_\lambda(\vec{q}, \vec{G}) \theta_\lambda(\vec{q}). \quad (2.17)$$

If we multiply Eq. (2.16) by $F_{\lambda'}^*(\vec{q}, \vec{G})$ and sum over \vec{G} , we obtain

$$\begin{aligned} \sum_{\lambda'} (\delta_{\lambda\lambda'} - X_{\lambda\lambda'}) [\sum_{\vec{G}} F_{\lambda'}^*(\vec{q}, \vec{G}) \epsilon_d^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')] \\ = F_{\lambda'}^*(\vec{q}, \vec{G}). \end{aligned} \quad (2.18)$$

Thus, the inversion of ϵ_d is reduced to the inversion of the 3×3 matrix $1 - X$, giving

$$E = (1 - X)^{-1}. \quad (2.19)$$

Substituting the solution for the sum in the square brackets in Eq. (2.18) into Eq. (2.16), we obtain

$$\begin{aligned} \epsilon_d^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= \delta_{\vec{G}, \vec{G}'} + \sum_{\lambda\lambda'} v_s(\vec{q} + \vec{G}) \theta_\lambda(\vec{q}) F_\lambda(\vec{q}, \vec{G}) \\ &\quad \times E_{\lambda\lambda'}(\vec{q}) F_{\lambda'}^*(\vec{q}, \vec{G}'). \end{aligned} \quad (2.20)$$

Armed with the knowledge of electron screening, we are now in a position to construct the dynamical matrix for phonons by using the microscopic theory¹⁹ (to be referred to as I). From Eq. (12.4), we have the dynamical matrix as a sum of two parts. One is due to the ion-ion interaction screened by the s, p electrons²¹:

$$\begin{aligned} \Phi_{\alpha\alpha'}^s(\vec{q}; \kappa\kappa') &= (M_\kappa M_{\kappa'})^{-1/2} \Omega_0^{-1} \sum_{\vec{G}} [e^{i\vec{G}\cdot(\vec{x}_\alpha - \vec{x}_{\kappa'})} \\ &\quad \times (q_\alpha + G_\alpha)(q_{\alpha'} + G_{\alpha'}) V_s(\vec{q} + \vec{G}; \kappa\kappa') \\ &\quad - \delta_{\kappa\kappa'} \sum_{\kappa''} e^{i\vec{G}\cdot(\vec{x}_\kappa - \vec{x}_{\kappa''})} G_\alpha G_{\alpha'} V_s(\vec{G}; \kappa\kappa'')], \end{aligned} \quad (2.21)$$

where $V_s(\vec{q} + \vec{G}; \kappa\kappa')$ is the effective ion-ion interaction screened by s, p electrons only,

$$\begin{aligned} V_s(\vec{q} + \vec{G}; \kappa\kappa') &= Z_\kappa Z_{\kappa'} v(\vec{q} + \vec{G}) + v(\vec{q} + \vec{G}, \kappa) \tilde{\chi}_s(\vec{q} + \vec{G}) \\ &\quad \times \epsilon_s^{-1}(\vec{q} + \vec{G}) v(\vec{q} + \vec{G}, \kappa'), \end{aligned} \quad (2.22)$$

$v(\vec{q} + \vec{G}; \kappa)$ being the electron-ion potential. The other part is the d -electron contribution:

$$\begin{aligned} \Phi_{\alpha\alpha}^d(\vec{q}; \kappa\kappa') &= (M_\kappa M_{\kappa'})^{-1/2} \Omega_0^{-1} [e^{i\vec{q}\cdot(\vec{r}_\kappa - \vec{r}_{\kappa'})} \\ &\times \sum_{\lambda\lambda'} \xi_{\alpha\lambda}(\vec{q}, \kappa) \theta_\lambda(\vec{q}) E_{\lambda\lambda'}(\vec{q}) \xi_{\alpha'\lambda'}^+(\vec{q}, \kappa') \\ &- \delta_{\kappa\kappa'} \sum_{\lambda\lambda'} \xi_{\alpha\lambda}(0, \kappa) \theta_\lambda(0) E_{\lambda\lambda'}(0) \xi_{\alpha'\lambda'}^+(0, \kappa')] , \end{aligned} \quad (2.23)$$

where

$$\xi_{\alpha\lambda}(\vec{q}, \kappa) = i \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}_\kappa} (q_\alpha + G_\alpha) v_s(\vec{q} + \vec{G}, \kappa) F_\lambda(\vec{q}, \vec{G}) , \quad (2.24)$$

$v_s(\vec{q} + \vec{G}, \kappa)$ being the electron-ion potential screened by the s, p electrons as in Eq. (2.13).

We have carried out the above procedure in the momentum space. We could equally well have done it in the configuration space, which has the virtue of being easier to interpret physically. The proper polarization part due to an electrical disturbance of wave vector \vec{q} is

$$\tilde{\chi}(\vec{r}, \vec{r}'; \vec{q}) = N^{-1} \sum_i \tilde{\chi}(\vec{r}, \vec{r}' - \vec{x}_i) e^{-i\vec{q}\cdot\vec{x}_i} . \quad (2.25)$$

The d -band contribution is of the separable form in RPA,

$$\tilde{\chi}_d(\vec{r}, \vec{r}'; \vec{q}) = \Omega \sum_\lambda \theta_\lambda(\vec{q}) F_\lambda(\vec{q}, \vec{r}) F_\lambda^*(\vec{q}, \vec{r}') , \quad (2.26)$$

where $F_\lambda(\vec{q}, \vec{r})$ is the Fourier transform of $F_\lambda(\vec{q}, \vec{G})$ of Eq. (2.5),

$$F_\lambda(\vec{q}, \vec{r}) = (2N)^{-1} \sum_{i\nu} e^{i\vec{q}\cdot\vec{x}_{i\nu}} |\varphi_\lambda(\vec{r} - \vec{x}_{i\nu})|^2 . \quad (2.27)$$

Thus, $F_\lambda(\vec{q}, \vec{r})$ is a density wave of d electrons of wave vector \vec{q} along the A -atom chains in the λ direction excited by the disturbance. The probability of such an excitation is measured by $\theta_\lambda(\vec{q})$.

The d -electron screening is measured by $X_{\lambda\lambda'}(\vec{q})$ in Eq. (2.17), which can be written

$$\begin{aligned} X_{\lambda\lambda'}(\vec{q}) &= \Omega \int d\vec{r} \int d\vec{r}' F_\lambda^*(\vec{q}, \vec{r}) v_s(\vec{r} - \vec{r}') \\ &\times F_{\lambda'}(\vec{q}, \vec{r}') \theta_{\lambda'}(\vec{q}) . \end{aligned} \quad (2.28)$$

This is read as the interaction of two d -electron density waves via the Coulomb interaction screened by the s, p electrons.

Equation (2.22) can be rewritten

$$\xi_{\alpha\lambda}(\vec{q}, \kappa) = \Omega \int d\vec{r} \left(\frac{\partial v_s(\vec{x}_\kappa - \vec{r}, \kappa)}{\partial x_{\alpha}} \right) F_\lambda(\vec{q}, \vec{r}) e^{-i\vec{q}\cdot\vec{x}_\kappa} , \quad (2.29)$$

which is the force on the κ ion due to the density wave along the A -atom chain in the λ direction.

Thus, we have given a theory for the d -electron screening in the tight-binding approximation. Its application is not limited to the β -W intermetallic compounds. The philosophy of our method is that for d electrons, it is not feasible to invert the dielectric function by a plane-wave expansion and that it is possible to construct a systematic scheme

of inversion in terms of the atomic (Wannier) functions. It is possible to extend the method to include overlap terms.

III. PHONON FREQUENCIES AT LONG WAVELENGTHS

A. Separation of Long-Range and Short-Range Interaction

We shall now examine the phonon behavior at long wavelength. To facilitate this, we separate the long-range and short-range parts of the interactions in the dynamical matrix given by (2.21) and (2.23) as shown in I.

The short-range part of the Coulomb interaction (and similarly the electron-ion potential) is defined by

$$\begin{aligned} \vartheta(\vec{q} + \vec{G}) &= v(\vec{q} + \vec{G}) \text{ if } \vec{G} \neq 0 \\ &= 0 \text{ if } \vec{G} = 0 . \end{aligned} \quad (3.1)$$

We also denote the corresponding dielectric function, electron-density response, etc., which do not contain the long-range part $v(\vec{q})$ by carets over the appropriate symbols.

Thus, the d -electron polarization is composed of

$$X_{\lambda\lambda'}(\vec{q}) = x_{\lambda\lambda'}(\vec{q}) + \hat{X}_{\lambda\lambda'}(\vec{q}) , \quad (3.2)$$

where

$$x_{\lambda\lambda'}(\vec{q}) = F_\lambda^*(\vec{q}, 0) v_s(\vec{q}) F_{\lambda'}(\vec{q}, 0) \theta_{\lambda'}(\vec{q}) , \quad (3.3)$$

and $\hat{X}_{\lambda\lambda'}(\vec{q})$ is given by Eq. (2.17) with \hat{v}_s in place of v_s , i. e., excluding the $\vec{G}=0$ term. The d -electron screening matrix is separated as

$$E = \hat{E} + \hat{E} x E , \quad (3.4)$$

where

$$\hat{E} = (1 - \hat{X})^{-1} . \quad (3.5)$$

Similarly,

$$\xi_{\alpha\lambda}(\vec{q}, \kappa) = i q_\alpha v_s(\vec{q}, \kappa) F_\lambda(\vec{q}, 0) + \hat{\xi}_{\alpha\lambda}(\vec{q}, \kappa) . \quad (3.6)$$

The modified dynamical matrix Eq. (13.1) may be written in the form of Eq. (12.11),

$$\begin{aligned} C_{\alpha\alpha'}(q; \kappa\kappa') &= (M_\kappa M_{\kappa'})^{-1/2} \Omega_0 \{ q_\alpha q_{\alpha'} [Z_\kappa Z_{\kappa'} v(q) \\ &- v(q, \kappa) v(q, \kappa') / v(q)] \\ &+ Z_\alpha^\dagger(q, \kappa) Z_{\alpha'}(q, \kappa') v(q) / \epsilon(q) \} \\ &+ \hat{C}_{\alpha\alpha'}^s(q; \kappa\kappa') + \hat{C}_{\alpha\alpha'}^d(q; \kappa\kappa') , \end{aligned} \quad (3.7)$$

where \hat{C}^s and \hat{C}^d are short-range counterparts of Eqs. (2.21) and (2.23), respectively, multiplied by $e^{-i\vec{q}\cdot(\vec{r}_\kappa - \vec{r}_{\kappa'})}$.

From Eq. (12.12), the effective charge of the sublattice is given by

$$\begin{aligned} Z_\alpha(\vec{q}, \kappa) &= -i q_\alpha v(\vec{q}, \kappa) / v(q) + \sum_{\lambda\lambda'} \theta_\lambda(\vec{q}) F_\lambda(\vec{q}, 0) \\ &\times \hat{E}_{\lambda\lambda'}(\vec{q}) \hat{\xi}_{\alpha\lambda}^+(\vec{q}, \kappa) . \end{aligned} \quad (3.8)$$

The dielectric function $\epsilon(\vec{q})$ defined in Eq. (12.9) is now

$$\epsilon(\vec{q}) = 1 - v(\vec{q}) \tilde{\chi}_s(\vec{q}, \vec{q}) - v(q) \tilde{\chi}_d(\vec{q}, \vec{q}) , \quad (3.9)$$

where, by Eqs. (2.11) and (2.20),

$$\hat{\chi}_d(\vec{q}, \vec{q}) = \sum_{\lambda\lambda'} \theta_\lambda(\vec{q}) F_\lambda(\vec{q}, 0) \hat{E}_{\lambda\lambda'}(\vec{q}) F_{\lambda'}^*(\vec{q}, 0). \quad (3.10)$$

Each term in the expression (3.7) for the modified dynamical matrix can be expanded in powers of \vec{q} .

B. Phonon Frequencies at Zero Wave Vector

At $\vec{q}=0$, we verify from Eq. (3.8) the general property that

$$Z_\alpha(0, \kappa) = 0. \quad (3.11)$$

Therefore, the dynamical matrix is given by the short-range parts in Eq. (3.7) and is covariant under the full symmetry group of the β -W structure,²² which is $O_h^3(Pm3n)$. The phonon polarization vectors can be classified by symmetry by the usual group-theoretic method.²³ They are listed in Table I.²⁴ The dynamical matrix is also considerably simplified by symmetry. With the help of Table I, the eigenvalues are easily obtained.

Consider the d -band contribution to the dynamical matrix. From Eq. (2.9),

$$\theta_\lambda(0) = \theta(0). \quad (3.12)$$

Strictly speaking, at $q=0$, $\theta(0)$ vanishes for any finite ω . Thus, there is no d -electron contribution to the zero-wave-vector optical modes, which, therefore, have no temperature variation in the harmonic approximation. In the following, we shall calculate the electronic contribution to the phonon frequency in the adiabatic approximation, that is, we put $\omega=0$ in Eq. (2.9), hence it follows that $\theta(0)$ is nonvanishing. There are two reasons for calculating the zero-wave-vector phonon frequencies in the adiabatic limit. First, it may apply to the optical modes with small but finite q which makes the excitation energy of the d -electron-hole pair $\mathcal{E}_{\lambda\vec{k},\vec{q}} - \mathcal{E}_{\lambda\vec{k}}$ in Eq. (2.9) much larger than the phonon frequency ω . The wave vector q has to be sufficiently small so that the phonon frequency in the adiabatic limit does not vary greatly from zero wave vector to q . This will not be true if, for example, q becomes comparable with the diameter of the d -electron Fermi surface in the same direction. Second, the zero-wave-vector phonons in the adiabatic limit occur in the elastic-wave coupling to the optical modes which we shall study in Sec. III C.

By cubic symmetry, the d -electron polarization $\hat{X}_{\lambda\lambda'}(0)$ has only two independent components:

$$\begin{aligned} \hat{X}_{\lambda\lambda'}(0) &= X_{11} \quad \text{if } \lambda = \lambda' \\ &= X_{12} \quad \text{if } \lambda \neq \lambda'. \end{aligned} \quad (3.13)$$

Hence, the same is true of the d -electron screening tensor $\hat{E}_{\lambda\lambda'}$ and

$$E_{11} - E_{12} = 1/(1 - X_{11} + X_{12}), \quad (3.14)$$

$$E_{11} + 2E_{12} = 1/(1 - X_{11} - 2X_{12}).$$

The force of $\vec{q}=0$ density wave in A atoms along λ direction $\xi_{\alpha\lambda}(0, \kappa)$ as given by Eq. (2.24) or (2.29), acting on the κ atom, is nonvanishing only if the κ atom is an A atom in a chain running in a direction other than λ . The forces on the consecutive atoms in λ' ($\neq \lambda$) chain are equal in magnitude and in opposite directions along the λ' chain. Let us put, say,

$$\xi_{y1}(0, 3) = \sigma. \quad (3.15)$$

By putting together the simplified forms of the quantities given by Eqs. (3.14) and (3.15) in Eq. (2.23), we find that in the d -band contribution to the dynamical matrix, the only nonzero elements are

$$\begin{aligned} C_{xy}^d(0; 13) &= -\theta(0)\sigma^2(E_{11} - E_{12})/M_A\Omega_0, \\ C_{xx}^d(0; 12) &= -C_{xx}^d(0; 11) = 2C_{xy}^d(0; 13), \end{aligned} \quad (3.16)$$

and the others which can be obtained from these by symmetry operations of the O_h^3 group. The force constants between two A atoms are nonzero only for components in the directions of the chains to which these atoms belong, respectively. There is no d -band contribution that affects the oscillation of a B atom.

From Eq. (3.16) and Table I, we deduce that the three $\alpha\Gamma_{15}$ modes are the acoustic branches with zero frequency and that no optical modes except the two Γ_{12} modes have d -band contribution. The square of the frequency of the Γ_{12} modes is the sum of two contributions

$$\omega^2(\Gamma_{12}) = \omega_s^2(\Gamma_{12}) + \omega_d^2(\Gamma_{12}), \quad (3.17)$$

where the d -band contribution

$$\omega_d^2(\Gamma_{12}) = 6\theta(0)\sigma^2(E_{11} - E_{12})/M_A\Omega_0. \quad (3.18)$$

TABLE I. Polarization vectors at Γ . The three columns under each value of κ are for the three Cartesian directions. The vectors are not normalized. For Γ_{15} , Γ_{25} , Γ_{15}' , and Γ_{25}' which have threefold degeneracies, only one of the three polarization vectors is given. ${}^{\beta}\Gamma_{15}$, ${}^{\gamma}\Gamma_{15}$, ${}^{\alpha}\Gamma_{25}$, ${}^{\beta}\Gamma_{25}$ are not, in general, eigenvectors. $A = (M_B/M_A)^{1/2}$, $B = -3(M_A/M_B)^{1/2}$.

κ	1	2	3	4	5	6	7	8
${}^{\alpha}\Gamma_{15}$	100	100	100	100	100	100	A00	A00
${}^{\beta}\Gamma_{15}$	100	100	100	100	100	100	B00	B00
${}^{\gamma}\Gamma_{15}$	$\bar{2}00$	$\bar{2}00$	100	100	100	100	000	000
${}^{\alpha}\Gamma_{25}$							100	$\bar{1}00$
${}^{\beta}\Gamma_{25}$			100	100	$\bar{1}00$	$\bar{1}00$		
Γ_2	100	$\bar{1}00$	010	0 $\bar{1}0$	001	00 $\bar{1}$		
Γ_{12}	200	$\bar{2}00$	0 $\bar{1}0$	010	00 $\bar{1}$	001		
Γ_{12}			010	0 $\bar{1}0$	00 $\bar{1}$	001		
Γ_{15}'			001	00 $\bar{1}$	010	0 $\bar{1}0$		
Γ_{25}'			001	00 $\bar{1}$	0 $\bar{1}0$	010		

It is easy to see physically the above conclusion of no d -band contribution to the optical modes except Γ_{12} . From Table I, we see that all modes of Γ_{15} or Γ_{25} symmetry involve rigid displacements of A -atom chains. Such motion cannot excite d electrons since in the tight-binding approximation adopted here, the d bands depend only on overlaps from neighboring sites in the same chain of A atoms. Modes of Γ'_{15} and Γ'_{25} symmetry involve rotation of pairs of A atoms about an axis perpendicular to the direction of the chain. To first order, this motion does not change the atomic spacing of the chain and, therefore, does not excite the d electrons. Only modes of Γ_2 and Γ_{12} symmetry involve oscillations of A atoms against each other in the same chain, which excite the d electrons. However, Γ_2 , being a nondegenerate mode, has cubic symmetry which makes the d -band contributions from the chains running in different directions cancel one another.

Of all the previous theoretical works on the lattice dynamics of A_3B compounds mentioned in the Introduction, only that of Klein and Birman¹² considered the optical modes. They concluded that at 0 °K, the Γ_{15} and Γ_{25} modes may become unstable for appropriate values of the density of states because of the overscreening by the d electrons. These authors started from the microscopic theory and the tight-binding approximation for the d bands in much the same way as ours. However, they used the diagonal approximation ($\vec{G} = \vec{G}'$ only) for the inverse dielectric function. We have shown in Sec. II that a careful inversion of the dielectric function gives nondiagonal terms for the d -band transitions. We believe that the diagonal approximation is inappropriate and that it leads Klein and Birman to the erroneous conclusion.

In the harmonic approximation, the only temperature dependence of the phonon frequency is via the temperature dependence of the electron occupation in the density response. For the s , p bands, the temperature dependence of the highly degenerate Fermi gas is negligible. For the d bands, because of the proximity of the Fermi level to the band edge, the temperature dependence of the electron polarization, as given by Eq. (2.9), is quite pronounced. Thus, the d -band contribution to the phonon frequency is the only source of temperature variation in the harmonic approximation. Therefore, we conclude that of all the long-wavelength optical modes, only Γ_{12} is temperature dependent.

C. Elastic Constants

We obtain the elastic constants from the sound velocities determined by the frequencies of the acoustic modes in the long-wavelength limit, following the procedure in I. We limit the wave vector q to be sufficiently small compared with the

diameter of the d -electron Fermi surface, such that a power-series expansion in q is valid. Because the sound velocity is small compared with the d -electron Fermi velocity, the adiabatic approximation is appropriate.

Because of the cubic symmetry, there are only three independent elastic constants:

$$c_{11} = [xx, xx] + (xx, xx), \quad (3.19a)$$

$$c_{12} = 2[xy, xy] - [yy, xx] + (xx, yy), \quad (3.19b)$$

$$c_{44} = [xx, yy] + (xy, xy) \quad (3.19c)$$

from Eqs. (I3.11)–(I3.14).

The round brackets ($\alpha\gamma, \beta\delta$) are contributions from the sublattice movement when the crystal is subjected to a homogeneous deformation. From Eq. (I3.14), they contain terms of the form $\sum_{\kappa\kappa'} w_{\alpha'}(\kappa' | O_J) C_{\alpha'\alpha\gamma}^{(1)}(\kappa'\kappa) M_{\kappa}^{1/2}$, where $C^{(1)}$ is the coefficient of the linear q term in the expansion of the modified dynamical matrix and $w_{\alpha'}(\kappa' | O_J)$ is the polarization vector of $\vec{q} = O, J$ phonon mode. By symmetry arguments, we find that the optical mode J must be in $\Gamma_{15} \times \Gamma_{15} = \Gamma_1 + \Gamma_{12} + \Gamma'_{15} + \Gamma'_{25}$. Indeed, we have deduced that

$$(xx, xx) = -4 \left[\sum_{\kappa} C_{xyy}^{(1)}(1\kappa) M_{\kappa}^{1/2} \right]^2 / \Omega_0 \omega^2(\Gamma_{12}), \quad (3.20a)$$

$$(xx, yy) = -\frac{1}{2}(xx, xx), \quad (3.20b)$$

$$(xy, xy) = -4 \left[\sum_{\kappa} C_{yyx}^{(1)}(1\kappa) M_{\kappa}^{1/2} \right]^2 / \Omega_0 \omega^2(\Gamma'_{25}). \quad (3.20c)$$

Actually, (xy, xy) contains coupling to the Γ'_{15} and Γ'_{25} modes, involving the squares of the difference and the sum, respectively, of the two terms $\sum_{\kappa} C_{xyy}^{(1)}(1\kappa) M_{\kappa}^{1/2}$ and $\sum_{\kappa} C_{yyx}^{(1)}(1\kappa) M_{\kappa}^{1/2}$, which are equal as a consequence of the infinitesimal rotational invariance and the equilibrium condition.²⁵

For a power-series expansion of the dynamical matrix $C_{\alpha\alpha'}(\vec{q}; \kappa\kappa')$ given by Eq. (3.7), we start with

$$\hat{\xi}_{\alpha\lambda}(q, \kappa) = \hat{\xi}_{\alpha\lambda}^{(0)}(\kappa) + iq_{\beta} \hat{\xi}_{\alpha\beta\lambda}^{(1)}(\kappa) + \dots, \quad (3.21)$$

where summation over repeated Greek indices is understood. From the considerations in Sec. III B, we have

$$\sum_{\kappa'} \hat{\xi}_{\alpha\lambda}^{(0)}(\kappa) = 0. \quad (3.22)$$

A similar expansion for the effective charge $Z_{\alpha}(q, \kappa)$ gives zero values for $Z_{\alpha}^{(0)}(\kappa)$, which is just Eq. (3.11), and

$$Z_{\alpha\beta}^{(1)}(\kappa) = Z_{\kappa} \delta_{\alpha\beta} - \theta(0)(E_{11} + 2E_{12}) \sum_{\lambda} \hat{\xi}_{\alpha\beta\lambda}^{(1)}(\kappa), \quad (3.23)$$

where Z_{κ} is the bare ionic charge and $E_{11} + 2E_{12}$ is the d -electron screening of a bulk wave, given by Eq. (3.14). Also, from Eq. (3.10),

$$\tilde{\chi}(0, 0) = \tilde{\chi}_s(0) + 3\theta(0)(E_{11} + 2E_{12}). \quad (3.24)$$

The short-range parts \hat{C}^s and \hat{C}^d of the dynamical matrix, by Eq. (I3.2), can be expressed in terms of the respective T^s and T^d matrices as follows:

$$\hat{C}_{\alpha\alpha'}(\vec{q}; \kappa\kappa') = (M_\kappa M_{\kappa'})^{-1/2} [T_{\alpha\alpha'}(\vec{q}; \kappa\kappa') - \delta_{\kappa\kappa'} \sum_{\kappa''} T_{\alpha\alpha'}(0; \kappa\kappa'')] \quad (3.25)$$

The expansion of T^s is straightforward using Eq. (2.21). In the expansion of T^d using Eq. (2.23), the terms which finally contribute to the elastic constants involve $\theta(q)$ and $\hat{E}_{\lambda\lambda}(\vec{q})$ only to zeroth order and $\hat{\xi}_{\alpha\lambda}(\vec{q}, \kappa)$ to first order, because the elastic constants involve sums of the coefficients of T^d over κ and because of Eq. (3.22).

The electron-ion potential is separated out as

$$v(\vec{q}; \kappa) = -Z_\kappa v(q) + v_R(q, \kappa) \quad (3.26)$$

Using the formulas in Sec. III of I, after some tedious manipulations, we obtain the expressions for the elastic constants,

$$\begin{aligned} c_{11} - c_{12} = & \frac{1}{2} [\{xx, xx\} + \{yy, xx\} - 2\{xy, xy\}] \\ & + \theta(0)(E_{11} - E_{12}) \{ \Omega_0^{-1} \sum_{\kappa} [\hat{\xi}_{xx1}^{(1)}(\kappa) - \hat{\xi}_{yy1}^{(1)}(\kappa)] \}^2 \\ & - 6 [\Omega_0 M_A \omega^2(\Gamma_{12})]^{-1} [\sum_{\kappa} T_{xy}^{s(1)}(1\kappa)] \\ & + \theta(0)(E_{11} - E_{12}) \sigma \Omega_0^{-1} \sum_{\kappa} [\hat{\xi}_{xx1}^{(1)}(\kappa) - \hat{\xi}_{yy1}^{(1)}(\kappa)]^2, \end{aligned} \quad (3.27)$$

$$\begin{aligned} \frac{1}{3}(c_{11} + 2c_{12}) = & \frac{1}{6} [\{xx, xx\} + 4\{xy, xy\} - 2\{yy, xx\}] \\ & + 2\Omega_0^{-2} \sum_{\kappa\kappa'} v_R(0, \kappa) Z_\kappa Z_{\kappa'} \\ & + (3\Omega_0^2)^{-1} \theta(0)(E_{11} + 2E_{12}) [\sum_{\lambda\kappa} \hat{\xi}_{xx\lambda}(\kappa)]^2 \\ & - [\Omega_0^2 \hat{\chi}(0, 0)]^{-1} [\sum_{\kappa} Z_\kappa \\ & - \theta(0)(E_{11} + 2E_{12}) \sum_{\lambda\kappa} \hat{\xi}_{xx\lambda}(\kappa)]^2, \end{aligned} \quad (3.28)$$

$$c_{44} = \frac{1}{2} \{xx, yy\} - 4 [\Omega_0 M_A \omega^2(\Gamma'_{25})]^{-1} [\sum_{\kappa} T_{yyx}^{s(1)}(1\kappa)]^2, \quad (3.29)$$

where

$$\{ \alpha\beta, \gamma\delta \} = \Omega_0^{-1} \sum_{\kappa\kappa'} T_{\alpha\beta\gamma\delta}^{s(2)}(\kappa\kappa'). \quad (3.29')$$

In contrast with the previous works⁹⁻¹¹ on the elastic constants of the β -W compounds, these formulas include (1) the contribution due to sublattice motion, the significance of which for the structural phase transition we shall discuss later, and (2) the d -electron interaction which provides quite different screening for different elastic modes.

There is evidence that the density of states at the Fermi level is much greater for the d band than for the s band.^{10,17} Then, the bulk modulus is approximately given by

$$\begin{aligned} \frac{1}{3}(c_{11} + 2c_{12}) = & \frac{1}{6} [\{xx, xx\} + 4\{xy, xy\} - 2\{yy, xx\}] \\ & + 2\Omega_0^{-1} \sum_{\kappa\kappa'} Z_\kappa Z_{\kappa'} v_R(0, \kappa) \\ & + (2/3\Omega_0^2) (\sum_{\kappa} Z_\kappa) [\sum_{\lambda\kappa} \hat{\xi}_{xx\lambda}^{(1)}(\kappa)]. \end{aligned} \quad (3.30)$$

Thus, we have shown that the bulk modulus is very weakly temperature dependent because of the high density of states at the Fermi level of the d band. Because we have included the electron screening carefully, we obtain the electronic contribution to the bulk modulus which is, roughly speaking, inversely proportional to the density of states. Our reason for the weak temperature dependence is different from that of Barisic and Labbe⁹ who ascribed it to the small number of electrons in the d band.

The shear modulus c_{44} is completely independent of the d electrons and is, therefore, temperature independent within the harmonic approximation. The c_{44} shear mode involves the change of relative angle between the A -atom chains without changing their spacings, which cannot excite the d electrons in the tight-binding approximation.⁹

The shear modulus $c_{11} - c_{12}$ has three terms in Eq. (3.27). The first term is due to the direct ion-ion interaction screened by the s , p electrons. The second term is the d -band contribution and is temperature dependent. The third term is the contribution of sublattice motion of Γ_{12} symmetry. It is temperature dependent via the coupling term as well as the optical-mode frequency.

D. Numerical Estimates

We give an approximate evaluation for the two most interesting quantities, namely, $\omega(\Gamma_{12})$ and $c_{11} - c_{12}$. We shall concentrate on Nb_3Sn . In reduced units, the properties of V_3Si are, on the whole, similar.

The polarization $\theta(0)$ can be evaluated from Eq. (2.9) with $\omega = 0$ and $q \rightarrow 0$ using the energy in Eq. (2.1).⁹ However, we follow a simpler procedure given in Ref. 10 of using a constant density of states $(1 - \alpha)N_0$ for the d band and another constant density of states αN_0 for the s band with a small α ($= 0.04$). This shows more clearly the temperature dependence of $\theta(0)$:

$$\theta(0) = - (8/3\Omega_0) N_0 F_0(T), \quad (3.31)$$

where

$$F_0(T) = 1 - e^{-T_F/T}, \quad (3.32)$$

T_F being the Fermi temperature measured from the d -band edge. We use two values of N_0 , 3.0 and 5.6 states/eV atom, obtained in Ref. 10 from resistivity and magnetic susceptibility measurements. The smaller value is more reasonable, being the bare density of states.²⁶ The values of T_F from Refs. 10 and 5 are 100 and 85°K, respectively.

We assume all unscreened interactions to be Coulombic. This amounts to neglecting the deviation of the electron-ion pseudopotential from the Coulomb potential v_R . The screening by s elec-

trons is treated in the Thomas-Fermi approximation for simplicity:

$$\epsilon_s(q) = 1 + q_{TF}^2 / q^2, \quad (3.33)$$

with

$$q_{TF}^2 = 4\pi e^2 \alpha N_0 (8/\Omega_0). \quad (3.34)$$

Despite the small value of α , the screening is quite drastic.

Such a crude approximation for the electron-ion interaction is satisfactory for the $c_{11} - c_{12}$ shear modulus but not for the other two elastic constants. For example, the neglect of the repulsive part $2\Omega_0^{-2} \sum_{\kappa\kappa'} Z_\kappa Z_{\kappa'} v_R(0, \kappa)$ in Eq. (3.28) renders the value of the bulk modulus negative. To raise the number to the experimental value by the repulsive part, we need an empty core pseudopotential²⁷ with a core radius of about 0.7 Å, a rather reasonable value. The importance of the repulsive part of the pseudopotential in the bulk modulus is similar to the case of alkali metals.^{27,28}

From the tight-binding approximation, it follows that the bulk modulus and the c_{44} shear modulus are weakly temperature dependent. Experimentally, this is true for V₃Si, but not for Nb₃Sn, for which c_{44} has a fairly large temperature dependence.⁵ One needs a better approximation for the d bands¹⁶ to explain this.

The d -electron wave function is taken to be the Slater form, Eq. (2.3), with $s = 0.74 \text{ Å}^{-1}$, approximately the atomic value. We have checked that the d -band contribution to the bulk modulus, third and fourth terms in Eq. (3.28), is indeed well approximated by the last term in Eq. (3.30).

We have calculated $\omega(\Gamma_{12})$ and $c_{11} - c_{12}$ as a function of temperature and compared the latter with experiment. The curves are shown in Ref. 15. The values of $c_{11} - c_{12}$ calculated roughly reproduced the measured behavior.⁵ The d -electron- d -electron screening in the shear wave is weak. For $N_0 = 3$, $-X_{11} + X_{12} = 0.21$. The coupling to the Γ_{12} optical mode is negligible at room temperatures but becomes quite important at low temperatures, sufficient to make a difference of over 10°K in the temperature at which the elastic constant becomes zero.

The frequency of the Γ_{12} mode is the highest of all branches, being the normal mode in which the nearest-neighbor niobium atoms oscillate against each other. It is, for example, $2.5 \omega(\Gamma'_{25})$. The decrease in $\omega(\Gamma_{12})$ in the adiabatic limit from room temperature to the lowest temperature is no more than 10%. We can say with some confidence that it does not become unstable at any temperature.

As was pointed out in Sec. IIIB, strictly at $q = 0$, $\omega(\Gamma_{12})$ is temperature independent. The adiabatic limit only applies if

$$\omega \ll \mathcal{E}_{\lambda\vec{k}+\vec{q}} - \mathcal{E}_{\lambda\vec{k}},$$

i. e., $q \gg 0.17\pi/a$, in our present estimates. The Fermi diameter in the [110] direction is about $0.2\pi/a$, where the Kohn effect may become important. Thus, for q less than $\frac{1}{10}\pi/a$, the optical mode close to Γ_{12} is more weakly temperature dependent than the adiabatic limit.

Barisic and Labbé⁹ have calculated the temperature dependence of $c_{11} - c_{12}$ for V₃Si and obtained good agreement with experiment, using the Slater coefficient $s = 0.27 \text{ Å}^{-1}$. We have found that such a small value used in our theory gives negligible d -band contribution. Barisic and Labbé^{9,14} have used the rigid-ion model in which the d electrons move rigidly with the atom. The electron-phonon interaction is due entirely to the change in the nearest-neighbor overlap. By contrast, we have included the d -electron polarization on each atom but neglected the overlap. Thus, Barisic and Labbé require a very spread-out d -electron wave function and we need a well-localized one. It is of interest to extend our calculations to include the overlap and estimate the relative magnitude of the two contributions.

IV. NATURE OF THE STRUCTURAL PHASE TRANSITION

In Sec. III, we have investigated the temperature dependence of the long-wavelength optical phonons and elastic constants in the cubic phase of the crystal. We now want to infer from these results the nature of the structural instability which causes a phase transition.

If the phase transition is second order, it will be due to the softening of an optical mode of symmetry^{29,30} Γ_{15} , Γ_{25} , or Γ'_{15} . We have shown that these optical modes do not have a strong d -band contribution and, therefore, do not go soft on cooling. There have been some experimental confirmations of this,^{6,30} although they are not conclusive.

We have shown that the Γ_{12} mode is temperature dependent but that in a rough evaluation, this high-frequency mode does not go soft. In fact, independent of any numerical calculation, from Eq. (3.27) for the shear modulus $c_{11} - c_{12}$, we see that if $\omega(\Gamma_{12})$ should become sufficiently small, the shear modulus would become negative first. The coupling of the acoustic mode to the long-wavelength optical mode would enable the optical mode to drive the acoustic mode unstable first. We conclude that no long-wavelength optical mode becomes unstable.

Our calculation shows that at a sufficiently low temperature, $c_{11} - c_{12}$ vanishes. This indicates that the phase transition is due to an acoustic instability, in agreement with previous authors.⁹⁻¹¹ However, we can go further and deduce from Sec. IIIC that associated with the acoustic mode is a tetragonal distortion of symmetry Γ_{12} . This is,

indeed, what Shirane and Axe⁷ found by elastic-neutron scattering of Nb₃Sn in the tetragonal phase. They have independently postulated that the Γ_{12} distortion is not due to the optical-mode softening but rather due to coupling with the $c_{11} - c_{12}$ shear mode which becomes unstable.

Therefore, the structural phase transition in Nb₃Sn must be first order. Although it is difficult

to infer this from specific-heat measurements directly, the combination of the lattice dynamical information above and the x-ray data³¹ should be convincing enough.

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